NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

61370

TECHNICAL REPORT 3115

THE COMPATIBILITY OF ADVANCED PACKAGEABLE ROCKET PROPELLANTS WITH MATERIALS OF CONSTRUCTION

J. D. CLARK
A. E. BOYCE
S. P. MOBLEY

OCTOBER 1963

AMCMS 5221.11.145.021
DA PROJECT 1A222901A201

PICATINNY ARSENAL
DOVER, NEW JERSEY

5 61370

TECHNICAL REPORT 3115

9 FINAL REP[redacted]T.

6 THE COMPATIBILITY OF ADVANCED
PACKAGEABLE ROCKET PROPELLANTS
WITH
MATERIALS OF CONSTRUCTION,

~~BY~~

10 by J. D. Clark,
A. E. Boyce and
S. P. Mobley,

11 OCT[redacted]63,

AMCMS 5221.11.145.021 16 DA PRO[redacted] 1A222901A203

REVIEWED BY: I. Forsten
I. FORSTEN
Chief, Liquid Rocket
Propulsion Laboratory

APPROVED BY: R W Vogel
R. W. VOGEL
Chief, Ammunition
Development Division

AMMUNITION ENGINEERING DIRECTORATE
PICATINNY ARSENAL
DOVER, NEW JERSEY

TABLE OF CONTENTS

ILLUSTRATIONS AND TABLES

INTRODUCTION

The object of this investigation was to determine ~~what~~ materials of construction ~~are~~ compatible with the rocket propellants ~~chlorine trifluoride~~ ClF_3 and Hydrazoid P for extended periods of time.

Certain Army missile propulsion needs can best be met by prepackaged liquid rocket power plants. These combine the convenience of handling of solid rocket power plants with the higher energy, flexibility, and controllability of liquid propellants. The classic pair of storable and packageable propellants, UDMH and IRFNA, however, are inadequate for future applications, and more energetic combinations must be sought.

Such a combination is Chlorine Trifluoride (CTF) and Hydrazoid P. The latter is a low freezing hydrazine mixture designed for use with a pure halogen oxidizer. It consists of four moles of monomethyl hydrazine, five of hydrazine, and one of perchloric acid, combined, of course, with the hydrazines.

Before these propellants can be used in a missile system, it is necessar to determine their long-time compatibility with materials of construction, particularly those which may be used in tankage. As Army requirements demand storability at any temperature between -65°F and +160°F, compatibility studies should emphasize the behavior of the materials investigated at the latter temperature. Here the conditions are the severest that will be met in service, and tests continuing weeks can reveal weaknesses that would not appear in years at room temperature. Thus, the two studies ~~which comprise the body of this~~ report emphasize the behavior of the propellants and the construction materials at the high temperature end of the storage range.

To pg - 4

It should be emphasized that these studies are directed at <u>long time</u>

storage. If it appears that Hydrazoid P, for instance, is incompatible with nickel over a period of weeks, this by no means implies that a nickel injector can not be used with this propellant. And if Teflon swells in contact with CTF, that does not mean that Teflon O-rings can not be used in the system plumbing, where they will be in contact with the propellant only for a time measured in seconds.

SUMMARY

A study has been made of the compatibility of various materials of construction with Hydrazoid P at room temperature and at 160°F, and with chlorine tri-fluoride at 160°C. The Hydrazoid P tests, which ran for 3600 hours, included the materials:

Stainless Steel	301	Inconel
	304	Nickel
	347	Tantalum
	17-7 PH	Titanium
Aluminum	2024	Polyethylene
	6061	Teflon
		Kel-F

The Chlorine trifluoride tests, which ran for 1728 hours, included the materials:

Stainless Steel	302	Aluminum	1100	Nickel
	304		2024	Copper
	316		5052	Inconel
	321		6061	Monel
	347		7075	Teflon.
			2-S	

Corrosion was monitored by weight loss of the specimen tested and by examination of its surface.

CONCLUSIONS

1. ~~The aluminum~~ al alloys, ~~tantalum~~ Ta, ~~titanium~~ Ti, polyethylene, and Teflon were unaffected by Hydrazoid P. ~~The~~ Inconel, ~~nickel,~~ Ni, and the stainless steels were appreciably corroded and the propellant was contaminated by corrosion products. The Kel-F swelled and blistered.

~~2.~~ None of the materials tested were appreciably corroded by ~~chlorine trifluoride.~~ ClF3.

RECOMMENDATIONS

~~1.~~ ~~Aluminum~~ al and ~~titanium~~ Ti. are recommended for tank materials for Hydrazoid P, and polyethylene and Teflon for O-ring material.

~~2.~~ Both ~~aluminum~~ al and stainless steel can be recommended as tank materials for ~~chlorine trifluoride.~~ ClF3. Teflon is the only non-metallic O-ring material recommended.

COMPATIBILITY STUDIES

Chlorine Trifluoride

The corrosivity of chlorine trifluoride (CTF), and its compatibility with materials of construction at room temperatures is quite well known but there is little information available as to its corrosive behavior at 70 to 80°C, (Reference 1). (In the region of the 160°F Mil. Spec. limit.) This study was intended to remedy, to some extent, this situation. The materials put under test were those which are compatible with CTF at room temperature and which might be expected to be so at 160°F. They include:

Stainless Steel	302	Aluminum	1100	Nickel
	304		2024	Copper
	316		5052	Inconel
	321		6061	Monel
	347		7075	Teflon
			2-S	

Kel-F was not tested because ambient temperature tests showed that it absorbed CTF which could not be removed by baking at 100°C.

The samples were in the form of thin strips approximately 3.2 cm x 1.3 cm and were exposed to the CTF in sealed SS cylinders (Figure 1) in a water bath held at 70-80 C. The CTF was used as received. It was nominally 99 percent pure, the major impurity being HF. Periodically, the samples were removed, examined, dried, and weighed. The average weight loss after 1728

hours is listed in Table 1, in milligrams per square centimeter of exposed surface, as is the average rate of corrosion, in mils per year.

The comparatively high corrosion rate of the SS 316 is attributed to the fact that the test cylinder containing it ruptured during the last test period, and some water was presumably picked up to increase the corrosion by the formation of HF.

The Teflon samples were exposed to the CTF at 160° F for 312 hours and absorbed approximately 1.5 weight per nt of CTF. This was almost completely driven off when the samples were baked at 100° C. There was no other discoverable effect on the Teflon.

It can be concluded that all of the metals tested, as well as Teflon, are satisfactory for long time service with CTF, since even at 160° F the corrosion rate is negligible for all practical purposes.

Liquid Rocket Propulsion Laboratory
Picatinny Arsenal, Dover, New Jersey

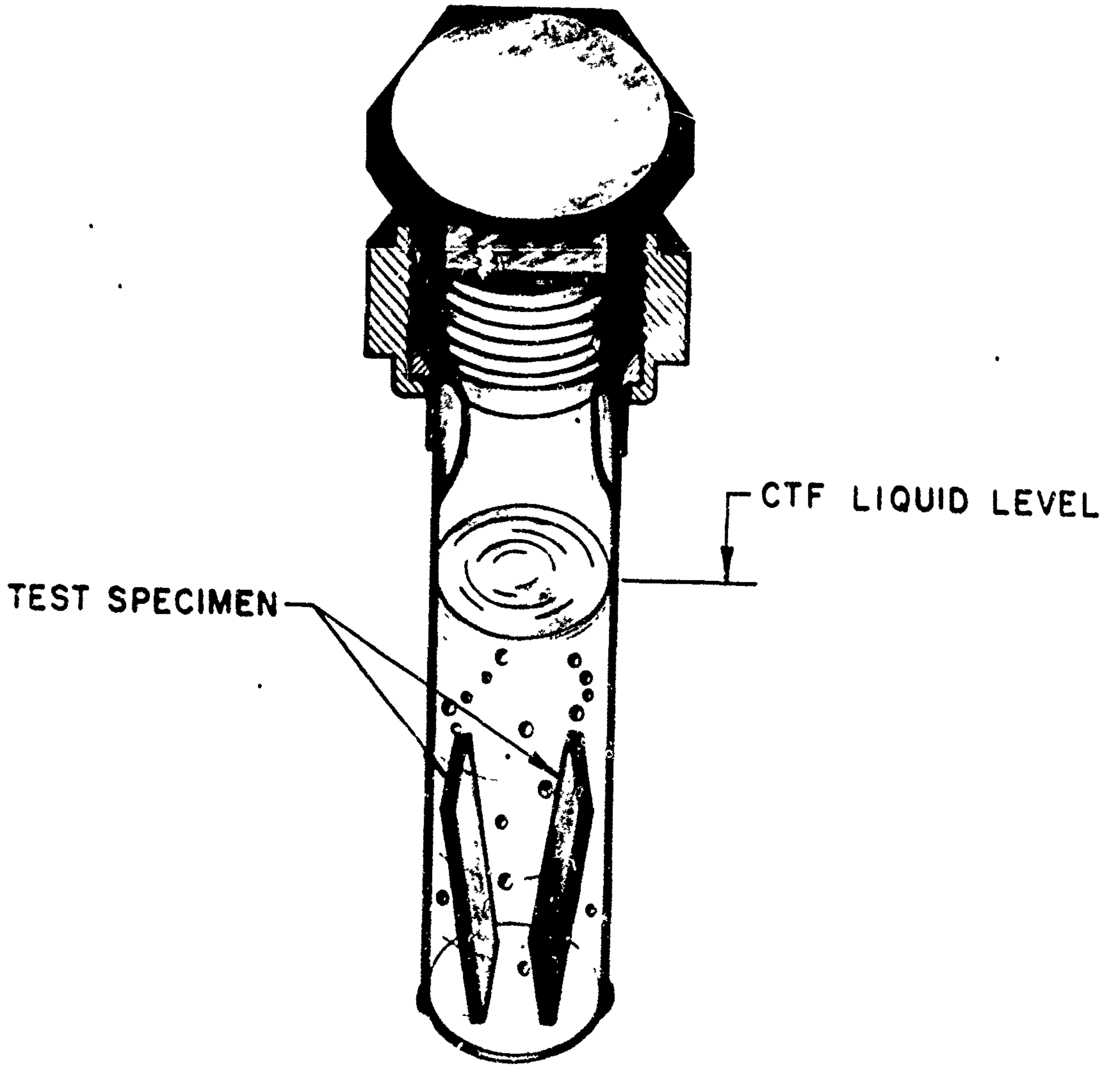


Fig 1. STAINLESS STEEL CTF COMPATIBILITY CYLINDER

TABLE 1: CORROSION IN CTF AT 160° F, 1728 HOURS.

	mg/cm^2	Mils/yr	
SS 302	0.23	0.05	
SS 316	1.60	0.41	
SS 304	0.35	0.09	
SS 321	0.14	0.04	
SS 347	0.23	0.06	
Al 1100	0.69	0.51	
Al 2024	0.05	0.03	
Al 5052	0.10	0.08	
Al 6061	0.08	0.06	
Al 7075	0.12	0.09	
Al 2S	0.05	0.04	
Nickel	0.55	0.12	
Copper	0.71	0.16	
Monel	0.26	0.11	(968 Hrs)
Inconel	0.14	0.05	(832 Hrs)

Hydrazoid P

Data on the corrosivity of Hydrazoid P and its compatibility with materials of construction has hitherto been lacking. The purpose of this study is to remedy this lack. The materials studied were those which were known to be compatible with hydrazine and might reasonably be expected to be compatible with Hydrazoid P, (Reference 2). They include:

Stainless Steel	301	Inconel
	304	Nickel
	347	Tantalum
	17-7 PH	Titanium
Aluminum	2024	Polyethylene
	6061	Kel-F
		Teflon

The samples were in the form of carefully cleaned thin strips, 3.9 x 2.2 cm, and were exposed to the Hydrazoid P in sealed glass flasks (Figure 2) at room temperature and in a water bath held at 70-72^{o}C (158-162^{o}F). The Hydrazoid P was made up in this laboratory, and assayed as follows:

Monomethyl Hydrazine	$CH_3N_2H_3$	39.0%
Hydrazine	N_2H_4	37.6%
Perchloric Acid	$HClO_4$	22.9%

The tests were continued for 150 days (3600 hours). Triplicate samples of each material were exposed. Periodically, they were removed from the test containers, washed, dried, examined, and weighed.

AA6061, AA2024, Titanium, Tantalum, Polyethylene, and Teflon were completely unaffected by the propellant in 150 days, at room temperature and at 160^{o}F. There was no observable weight change (less than 0.1mg) and no visible change of any sort, and these materials can be considered as completely compatible with Hydrazoid P and suitable for unlimited service with this propellant.

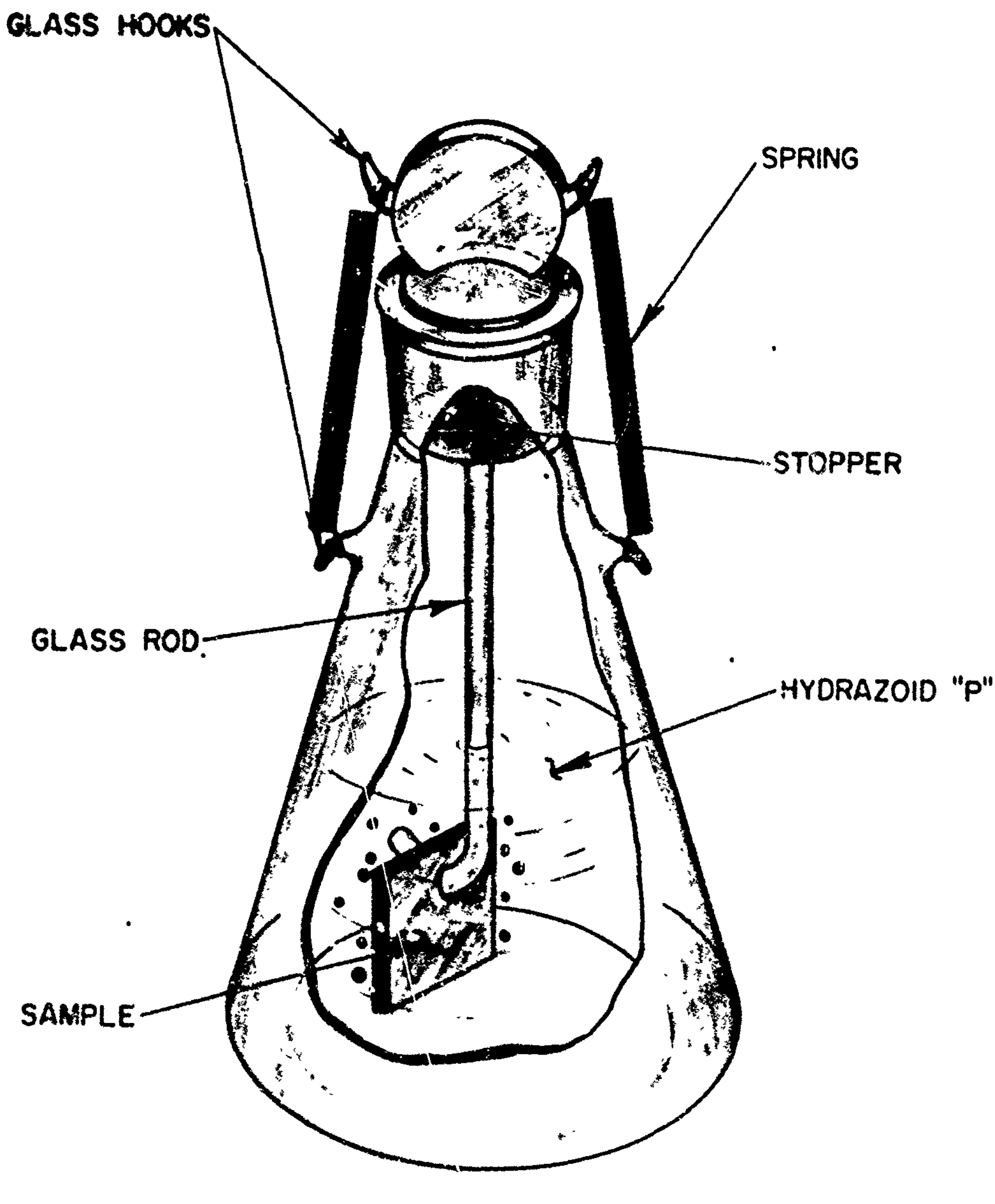


Fig 2. HYDRAZOID P COMPATIBILITY TEST

At 160°F, Kel-F turned dark brown, after ten days, but there was no othe observable change for the first 120 days except a slight increase in weight. Shortly thereafter the sample began to lose weight, its surface became pimpled and the propellant started to turn brown. The weight loss continued until the end of the test. A photomicrograph of the test sample after 150 days is shown in Figure 3. A similar, but much less marked effect wa noticed at room temperature. This attack upon Kel-F is reminiscent of a imilar effect noticed some ten years ago at Pt. Mugu, where Kel-F sheet intended for expul sion bags was completely disintegrated by aniline.

The nickel, the Inconel, and the four stainless steels were attacked by the propellant. The 150 day results are shown in Table 2, where the average corrosion is shown as mg/cm^2 per 150 days, and, assuming a constant, average corrosion rate, as mils/year.

The propellant was discolored, acquiring a pinkish-purple hue, whose intensity varied, naturally, with the extent of the corrosion. This is apparently due to the formation of a cation $Ni(N_2H_4)_x^{++}$ such as those reported by Kramer, (Reference 3). This cation is apparently a very strong base, since analysis of the propellant acting upon the nickel at 160°F, showed that in two weeks the apparent perchloric acid content had dropped by two percent. It appears probable that the high temperature corrosion of the nickel would have been considerably larger at the 150 day mark were it not for the depletion of the perchloric acid and the accumulation of corrosion products in the solution.

Photomicrographs of the nickel and Inconel specimens after 150 days at 160°F are shown in Figures 4 and 5.

It is apparent that neither nickel nor alloys containing considerable percentages of that metal are suitable container materials for the long-time storage of Hydrazoid P.

At 160° F, Kel-F turned dark brown, after ten days, but there was no other observable change for the first 120 days except a slight increase in weight. Shortly thereafter the sample began to lose weight, its surface became pimpled and the propellant started to turn brown. The weight loss continued until the end of the test. A photomicrograph of the test sample after 150 days is shown in Figure 3. A similar, but much less marked effect wa noticed at room temperature. This attack upon Kel-F is reminiscent of a imilar effect noticed some ten years ago at Pt. Mugu, where Kel-F sheet intended for expulsion bags was completely disintegrated by aniline.

The nickel, the Inconel, and the four stainless steels were attacked by the propellant. The 150 day results are shown in Table 2, where the average corrosion is shown as mg/cm^2 per 150 days, and, assuming a constant, average corrosion rate, as mils/year.

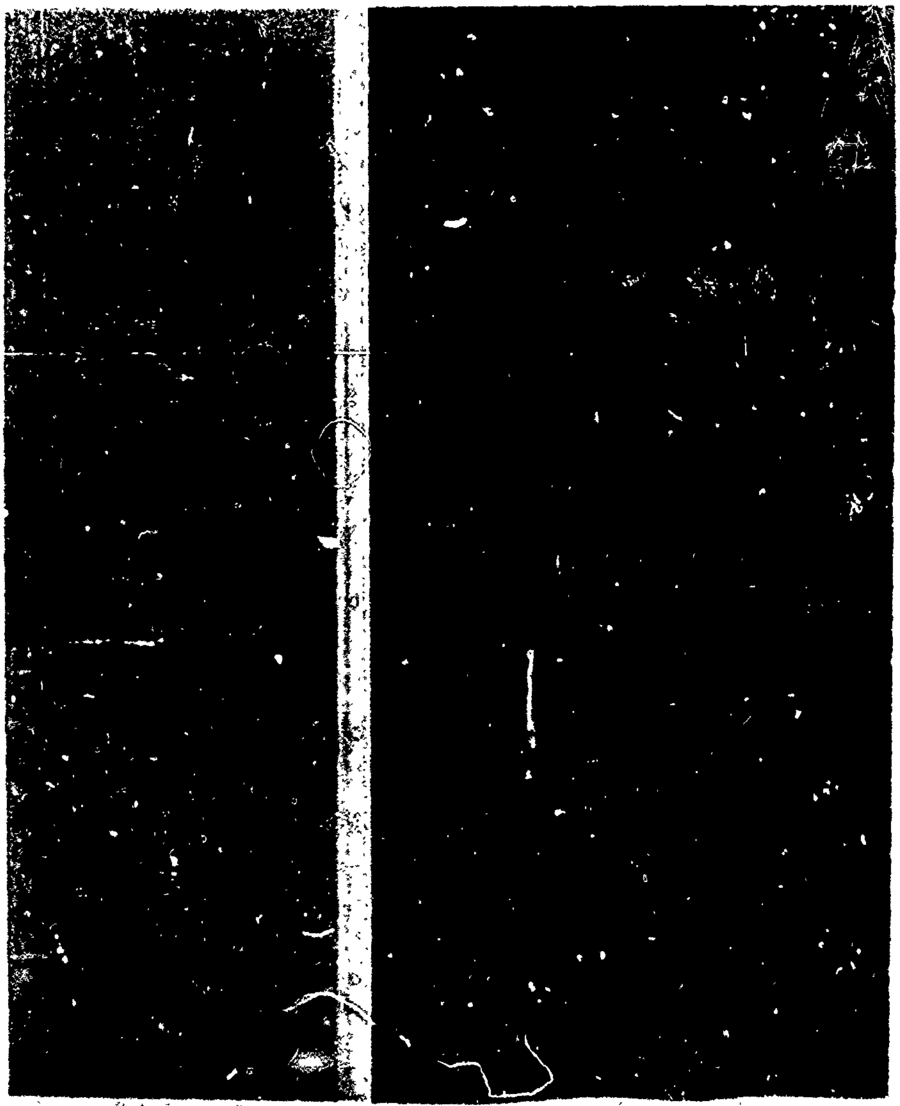
The propellant was discolored, acquiring a pinkish-purple hue, whose intensity varied, naturally, with the extent of the corrosion. This is apparently due to the formation of a cation $Ni(N_2H_4)_x^{++}$ such as those reported by Kramer, (Reference 3). This cation is apparently a very strong base, since analysis of the propellant acting upon the nickel at 160° F, showed that in two weeks the apparent perchloric acid content had dropped by two percent. It appears probable that the high temperature corrosion of the nickel would have been considerably larger at the 150 day mark were it not for the depletion of the perchloric acid and the accumulation of corrosion products in the solution.

Photomicrographs of the nickel and Inconel specimens after 150 days at 160° F are shown in Figures 4 and 5.

It is apparent that neither nickel nor alloys containing considerable percentages of that metal are suitable container materials for the long-time storage of Hydrazoid P.

TABLE 2: CORROSION IN HYDRAZOID P, 3600 HOURS.

	Ambient Temperature		160° F	
	mg/cm^2	Mils/yr	mg/cm^2	Mils/yr
Nickel	10.58	1.07	24.74	2.43
Inconel	6.98	0.81	13.73	1.40
SS 304	0.67	0.053	18.81	1.38
SS 301	0.58	0.042	10.15	0.79
SS 347	0.13	0.010	6.52	0.50
17-7 PH	0.72	0.046	6.52	0.42

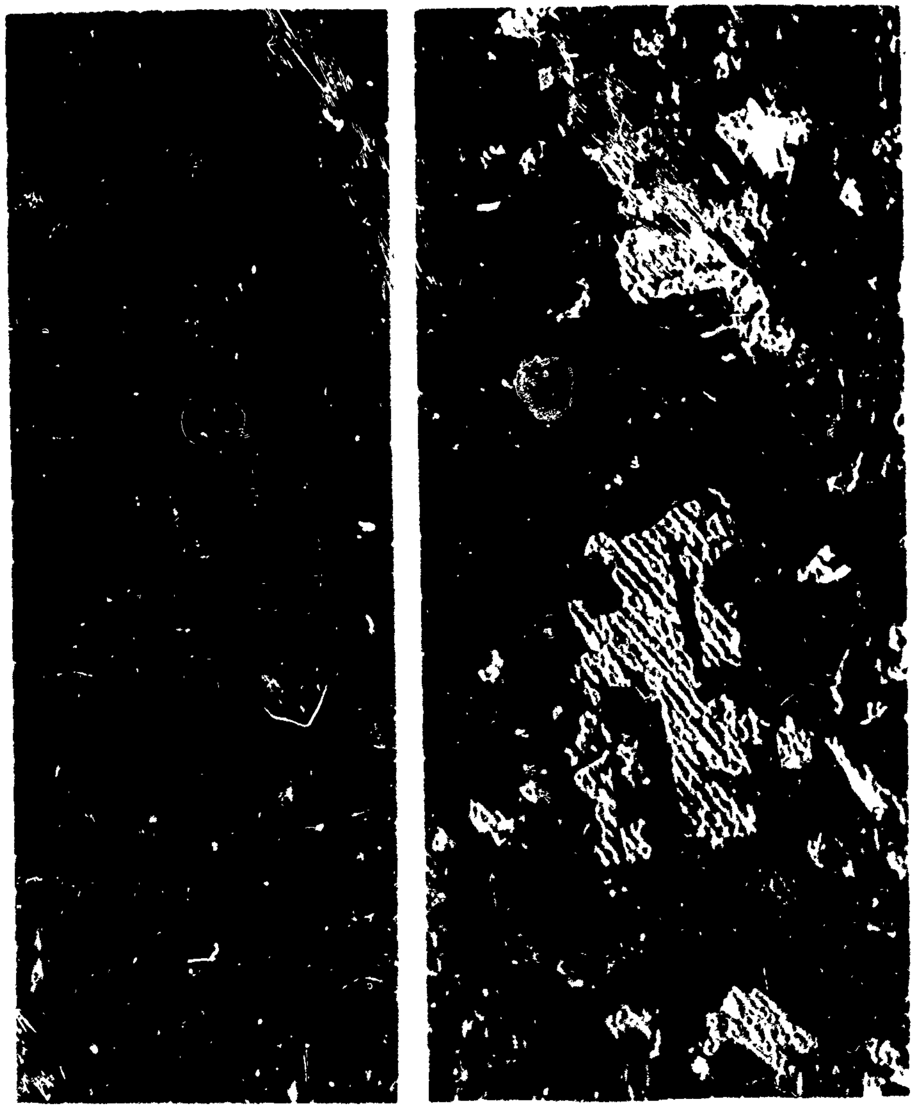


Control Sample

Kel F

Mag. 40 X

Fig 3. KEL-F AFTER 150 DAYS IN HYDRAZOID P AT 160° F



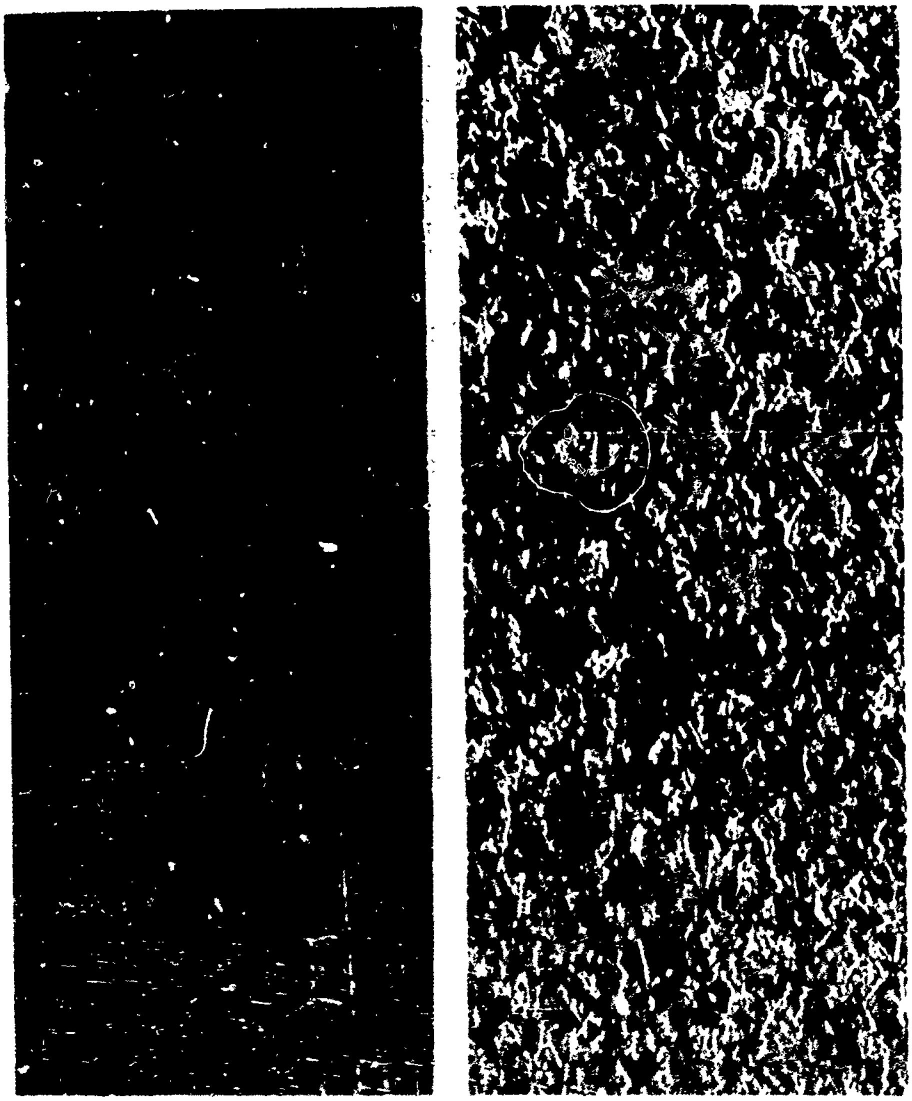
Control Sample

Nickel Sample

Mag. 40 X

Fig 4. NICKEL AFTER 150 DAYS IN HYDRAZOID P AT 160°F

Liquid Rocket Propulsion Laboratory
Picatinny Arsenal, Dover, New Jersey



Control Sample

Inconel Sample

Mag. 40 X

Fig 5. INCONEL AFTER 1:0 DAYS IN HYDRAZOID P AT 160° F

REFERENCES

1. Compatibility of CTF with Materials of Construction, Pennsalt Chemicals Corp., April 1961.

2. Hydrazine Handling Manual, Rocketdyne, R-3134, Sept 1961.

3. G. M. Kramer et al. The Effect of Various Materials upon the Stability of the Hydrazine - Hydrazine Nitrate - Water System, Frankford Arsenal, R-1100, Sept 1952.

DISTRUBITION LIST

No. of Copies	
20	Defense Documentation Center Cameron Station Alexandria, Virginia
5	Commanding Officer Picatinny Arsenal ATTN: SMUPA-VA6 Dover, New Jersey
1	Chief of Research and Development Missiles and Space Division Department of the Army ATTN: Maj. J. E. McCleary Washington 25, D. C.
1	Commanding General Ballistic Research Laboratories Aberdeen Proving Ground Maryland
6	Commanding General U. S. Army Missile Command Redstone Arsenal Huntsville, Alabama ATTN: Librarian Dr. M. Hall Dr. D. Sayles Dr. W. Wharton Mr. R. Rogers, Project Mgr, Lance Missile
1	Commanding General U. S. Army Weapons Command ATTN: Mr. W. G. Smith Rock Island, Illinois

No. of
Copies

1

Commanding Officer
Frankford Arsenal
ATTN: SMUFA
Philadelphia, Pennsylvania

1

Commanding Officer
Harry Diamond Laboratories
ATTN: AMXDO
Connecticut Ave & Van Ness St, N. W.
Washington 25, D. C.

1

Commanding Officer
U. S. Army Research Office (Durham)
ATTN: Librarian
Box CM
Duke Station, Durham, North Carolina

1

Commanding Officer
U. S. Army Signal Missile Support Agency
ATTN: STEMS
White Sands Missile Range, New Mexico

1

Commanding Officer
Watervliet Arsenal
ATTN: Librarian
Watervliet, New York

1

U. S. Army Engineering Research
and Development Laboratory
ATTN: Librarian
Fort Belvoir, Virginia

1

Aerojet-General Corporation
P. O. Box 296
ATTN: M. Grenier, Librarian
Azusa, California

1

Aerojet-General Corporation
Sacramento Plants, P. O. Box 1947
ATTN: R. G. Weitz, Head Tech Info Office
Sacramento 9, California

No. of Copies	
1	The Boeing Company Aero Space Division ATTN: R. R. Barber, Lib Ut Ch P. O. Box 3707 Seattle 24, Washington
~~10~~ 3	Chemical Propellant Information Agency The Johns Hopkins University Applied Physics Laboratory 8621 Georgia Avenue Silver Springs, Maryland
1	General Electric Company Aerothermochemistry Unit ATTN: G. G. Kutzko, Manager Combustion Applied Research Cincinnati 15, Ohio
1	Jet Propulsion Laboratory California Institute of Technology ATTN: Technical Reports Section 4800 Oak Grove Drive Pasadena, California
1	Lewis Research Center National Aeronautics and Space Administration ATTN: Librarian 31000 Brookpark Road Cleveland 35, Ohio
1	Lockheed Propulsion Company ATTN: Librarian P. O. Box 111 Redlands, California
1	National Aeronautics and Space Administration George C. Marshall Space Flight Center ATTN: Library Huntsville Alabama

No. of Copies	
1	New York University Department of Chemical Engineering ATTN: P. F. Winternitz New York 53, New York
1	Rocketdyne North American Aviation, Inc. 6633 Canoga Avenue ATTN: J. Silverman Canoga Park, California
1	Rohm and Haas Company Redstone Arsenal Research Division ATTN: Librarian Redstone Arsenal, Alabama
1	Thiokol Chemical Corporation Reaction Motors Division ATTN: Librarian Denville, N. J.
1	United Aircraft Corporation Pratt & Whitney Florida Research & Development ATTN: Library P. O. Box 2691 W. Palm Beach, Florida
1	Office of the Director of Defense Research & Eng. Director of Weapons System Evaluation Group Room 2E812, The Pentagon Washington 25, D. C.
2	Commander U. S. Naval Ordnance Test Station China Lake, California ATTN: Code 4538 Code 4522

No. of Copies	
1	Air Force Office of Scientific Research ATTN: Dr. Bernard T. Wolfson Washington 25, D. C.
1	Ling-Temco-Vought, Michigan P. O. Box 68 Village Station ATTN: Mr. Jim Green Warren, Michigan
1	Rocketdyne 6633 Canoga Ave ATTN: Mr. Jim Bates, LANCE Project Canoga Park, California

Accession No. ______________ AD ______________

Picatinny Arsenal, Dover, New Jersey

THE COMPATIBILITY OF ADVANCED PACKAGE-ABLE ROCKET PROPELLANTS WITH MATERIALS OF CONSTRUCTION

J. D. Clark, A. E. Boyce, S. P. Mobley

Technical Report 3115, October 1963, 16 pages, drawings, photographs, tables. Unclassified Report from the Liquid Propellant Section, Liquid Rocket Propulsion Laboratory of the Ammunition Engineering Directorate.

Compatibility of materials with chlorine trifluoride and Hydrazoid P for extended periods of time showed that Aluminum and titanium are recommended tank materials for Hydrazoid P using polyethylene and Teflon for O-ring ma-

(over)

UNCLASSIFIED

1. Liquid Propellant
2. Hydrazoid P
3. Chlorine trifluoride

I. Clark, J. D.
II. Boyce, A. E.
III. Mobley, S. P.
IV. Title

UNITERMS

Compatibility
Package
Rocket
Propellant
Liquid

UNCLASSIFIED

Accession No. ______________ AD ______________

Picatinny Arsenal, Dover, New Jersey

THE COMPATIBILITY OF ADVANCED PACKAGE-ABLE ROCKET PROPELLANTS WITH MATERIALS OF CONSTRUCTION

J. D. Clark, A. E. Boyce, S. P. Mobley

Technical Report 3115, October 1963, 16 pages, drawings, photographs, tables. Unclassified Report from the Liquid Propellant Section, Liquid Rocket Propulsion Laboratory of the Ammunition Engineering Directorate.

Compatibility of materials with chlorine trifluoride and Hydrazoid P for extended periods of time showed that Aluminum and titanium are recommended tank materials for Hydrazoid P using polyethylene and Teflon for O-ring ma-

(over)

UNCLASSIFIED

1. Liquid Propellant
2. Hydrazoid P
3. Chlorine trifluoride

I. Clark, J. D.
II. Boyce, A. E.
III. Mobley, S. P.
IV. Title

UNITERMS

Compatibility
Package
Rocket
Propellant
Liquid

UNCLASSIFIED

Accession No. ______________ AD ______________

Picatinny Arsenal, Dover, New Jersey

THE COMPATIBILITY OF ADVANCED PACKAGE-ABLE ROCKET PROPELLANTS WITH MATERIALS OF CONSTRUCTION

J. D. Clark, A. E. Boyce, S. P. Mobley

Technical Report 3115, October 1963, 16 pages, drawings, photographs, tables. Unclassified Report from the Liquid Propellant Section, Liquid Rocket Propulsion Laboratory of the Ammunition Engineering Directorate.

Compatibility of materials with chlorine trifluoride and Hydrazoid P for extended periods of time showed that Aluminum and titanium are recommended tank materials for Hydrazoid P using polyethylene and Teflon for O-ring ma-

(over)

UNCLASSIFIED

1. Liquid Propellant
2. Hydrazoid P
3. Chlorine trifluoride

I. Clark, J. D.
II. Boyce, A. E.
III. Mobley, S. P.
IV. Title

UNITERMS

Compatibility
Package
Rocket
Propellant
Liquid

UNCLASSIFIED

Accession No. ______________ AD ______________

Picatinny Arsenal, Dover, New Jersey

THE COMPATIBILITY OF ADVANCED PACKAGE-ABLE ROCKET PROPELLANTS WITH MATERIALS OF CONSTRUCTION

J. D. Clark, A. E. Boyce, S. P. Mobley

Technical Report 3115, October 1963, 16 pages, drawings, photographs, tables. Unclassified Report from the Liquid Propellant Section, Liquid Rocket Propulsion Laboratory of the Ammunition Engineering Directorate.

Compatibility of materials with chlorine trifluoride and Hydrazoid P for extended periods of time showed that Aluminum and titanium are recommended tank materials for Hydrazoid P using polyethylene and Teflon for O-ring ma-

(over)

UNCLASSIFIED

1. Liquid Propellant
2. Hydrazoid P
3. Chlorine trifluoride

I. Clark, J. D.
II. Boyce, A. E.
III. Mobley, S. P.
IV. Title

UNITERMS

Compatibility
Package
Rocket
Propellant
Liquid

UNCLASSIFIED

terials. Chlorine trifluoride is compatible with both Aluminum and stainless steel for tank materials, while Teflon is the only non-metallic O-ring material recommended.

UNCLASSIFIED

UNITERMS

Construction
Material
O-ring
Tank
Hydrazoid P
Chlorine Trifluoride
Teflon
Polyethylene
Aluminum
Steel
Stainless
Clark, J. D.
Boyce, A. E.
Mobley, S. P.

UNCLASSIFIED

terials. Chlorine trifluoride is compatible with both Aluminum and stainless steel for tank materials, while Teflon is the only non-metallic O-ring material recommended.

UNCLASSIFIED

UNITERMS

Construction
Material
O-ring
Tank
Hydrazoid P
Chlorine Trifluoride
Teflon
Polyethylene
Aluminum
Steel
Stainless
Clark, J. D.
Boyce, A. E.
Mobley, S. P

UNCLASSIFIED

terials. Chlorine trifluoride is compatible with both Aluminum and stainless steel for tank materials, while Teflon is the only non-metallic O-ring material recommended.

UNCLASSIFIED

UNITERMS

Construction
Material
O-ring
Tank
Hydrazoid P
Chlorine Trifluoride
Teflon
Polyethylene
Aluminum
Steel
Stainless
Clark, J. D.
Boyce, A. E.
Mobley, S. P.

UNCLASSIFIED

terials. Chlorine trifluoride is compatible with both Aluminum and stainless steel for tank materials, while Teflon i the only non-metallic O-ring material recommended.

UNCLASSIFIED

UNITERMS

Construction
Material
O-ring
Tank
Hydrazoid P
Chlorine Trifluoride
Teflon
Polyethylene
Aluminum
Steel
Stainless
Clark, J. D.
Boyce, A. E.
Mobley, S. P.

UNCLASSIFIED